

Incommensurate Antiferromagnetic Insulating State in (MDT-TS)(AuI₂)_xHideo YOSHIOKA^{1*}, Hitoshi SEO^{2,3†}, and Yuichi OTSUKA^{2,3‡}¹Department of Physics, Nara Women's University, Nara 630-8506²Condensed Matter Theory Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198³JST, CREST, 2-1 Hirosawa, Wako, Saitama 351-0198

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We theoretically study the metal-insulator transition in a molecular conductor (MDT-TS)(AuI₂)_x composed with an incommensurate ratio ($x = 0.441$), where the conduction band originated from the HOMO of donor MDT-TS molecules is incommensurately filled. We consider a two-dimensional Hubbard model taking account of anisotropic transfer integrals in the donor layer, under a periodic potential due to the anions (AuI₂)[−] which mismatches the donor lattice period, and investigate the ground state within mean-field approximation. An antiferromagnetic insulating state with induced charge disproportionation is obtained in the large U region; this corresponds to the incommensurate Mott insulating state predicted previously [H. Yoshioka *et al.*: J. Phys. Soc. Jpn. **74** (2005) 1922] based on a simplified one-dimensional model.

KEYWORDS: molecular conductors, Hubbard model, incommensurate filling, metal-insulator transition, Mott insulator, organic conductors

In recent years, molecular conductors with incommensurate (IC) composition ratios have been synthesized and their electronic properties are explored experimentally.^{1,2)} Among them, a series of isostructural compounds expressed as AB_x where A denote donor molecules such as MDT-TSF, MDT-ST, MDT-TS, and B are monovalent anions taking (AuI₂)[−] and (I₃)[−], have been systematically investigated.^{3–15)} They form quasi-two-dimensional crystal structures with alternatively stacking A and B layers. Since B takes closed shell configurations, the irrational values of $x \simeq 0.41 - 0.45$ result in irrational average valences for the donors A^{+x} ; then the conduction band composed of the HOMO of donors becomes incommensurately filled. The filling factors are $n_e = 2 - x$, slightly larger than 3/4-filling ($n_e = 3/2$) which would correspond to $x = 1/2$ (i.e., A_2B); in the hole picture, they are slightly smaller than quarter-filling.

As is naturally expected from such IC band fillings, most of these compounds show metallic behavior, and some undergo a superconducting transition with a maximum $T_c \simeq 4$ K.^{3–6,12,14)} However, exceptionally, (MDT-TS)(AuI₂)_x ($x = 0.441$) shows a metal-insulator crossover at $T_\rho = 85$ K where the temperature-dependence of the resistivity has a minimum.^{9,10,15)} With further decreasing the temperature, an antiferromagnetic (AF) transition takes place at $T_N = 50$ K. By applying external pressure, T_ρ decreases and a superconducting phase appears above $P_c = 10.5$ kbar. The fact that the insulating state does not accompany a magnetic order in the temperature range $T_\rho > T > T_N$ implies that the insulating behavior in this compound might be due to strong correlation, in spite of the IC filling where strong-coupling insulators are usually not expected. In contrast, Mott insulators and charge ordered insulators are frequently observed in typical molecular conductors with commensurate fillings, which are theoretically studied based on Hubbard-type models extensively.¹⁶⁾

A key to understand the origin of the insulating behavior in (MDT-TS)(AuI₂)_x is the fact that the anions B^- in these

materials are not randomly distributed: X-ray scattering experiments show that they form regular lattices with a different periodicity from that of donor lattices.^{4–6,11)} Owing to this mismatch in periodicities, the anions are expected to influence the electronic state in the donor HOMO band as a periodic potential. In fact, reconstructions of the Fermi surface by the anion potential in metallic compounds are observed by the Shubnikov-de Haas oscillations.^{7,13)}

Taken these facts together, a peculiar Mott insulating state in electronic systems with IC band filling has been theoretically proposed.^{17,18)} When the periodic anion potential is strong enough, the conduction band becomes effectively half-filled, since the filling does match the periodicity of monovalent anions that provide one hole per anion to the donors. As a result, the mutual Coulomb interaction between electrons on the donor lattice is expected to lead to a Mott insulating state. Its existence was confirmed within a simplified one-dimensional (1D) model which incorporates the IC filling as well as the anion potential, by using bosonization and perturbative renormalization group methods.¹⁷⁾ This strong-coupling insulating state, which is produced by the cooperative effect of anion potential and electronic correlation, is

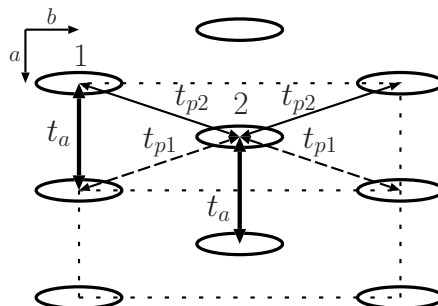


Fig. 1. Schematic representation of the two-dimensional donor layer in (MDT-TS)(AuI₂)_x. Ellipses denote MDT-TS molecules and the unit cell written by the dotted lines contains two equivalent molecules. The transfer integrals t_a , t_{p1} , and t_{p2} are represented by arrows.

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called as “IC Mott insulator” in order to distinguish it from the usual Mott insulator at half filling. In the former, the localized spins do not situate on the donor sites in a commensurate way but follow the periodicity of the anion potential; in the latter spin $1/2$ simply localizes on each site.

In the present paper, beyond the simplified 1D model, we study a two-dimensional Hubbard model with anisotropic transfer integrals between the donors which reflect the actual structure of (MDT-TS)(AuI₂)_x. Within mean-field approximation, we obtain self-consistent insulating solutions at large Coulomb interaction, considered as the IC Mott insulator, where the charge disproportionation induced by the anion potential coexists with AF ordering.

The model for (MDT-TS)(AuI₂)_x we consider is represented as

$$H = \sum_{\langle ij \rangle, \sigma} t_{ij} (c_{i, \sigma}^\dagger c_{j, \sigma} + \text{h.c.}) + U \sum_i n_{i, \uparrow} n_{i, \downarrow} + \sum_i v_i n_i, \quad (1)$$

where $c_{i, \sigma}^\dagger$ is the creation operator of the electron with spin $\sigma = \uparrow, \downarrow$ at the i -th donor site. The crystal structure and the hopping parameters t_{ij} in the donor layer are schematically shown in Fig.1. We set values of t_{ij} as those calculated by the extended Hückel method,¹⁰⁾ $t_a = 76.0$ meV, $t_{p1} = -7.9$ meV, and $t_{p2} = -26.3$ meV, and consider the on-site Coulomb interaction U for each donor site.

We assume that the potential from the anions, expressed as v_i , depends only on the coordinate along the a -axis in the respective columns, considering the fact that in the actual materials the anions align in this direction.^{5, 6, 9, 11)} Namely, we adopt the form:

$$v_i^{(1)} = \delta \cos(2\pi x \xi_i^{(1)}) \quad (2)$$

$$v_i^{(2)} = \delta \cos(2\pi x \{ \xi_i^{(2)} - 1/2 + \phi \}), \quad (3)$$

where $v_i^{(\mu)}$ and $\xi_i^{(\mu)}$ ($\mu = 1, 2$) express the anion potential and the coordinate along the a -axis for molecule i in the μ -th column of the unit cell; we take the intermolecular distance in this direction as $a = 1$. The strength of the anion potential is denoted by δ . Note that, from the chemical formula (MDT-TS)(AuI₂)_x, the anion periodicity is given by $1/x$. The relative position between the two anion columns, which determine the phase ϕ , is taken as 0 in this work, but the overall features below remain unchanged for different values of ϕ . Since the anions become monovalent by subtracting electrons from the donor layer, the filling factor of the donor sites in terms of holes, $n_h = 2 - n_e$, coincides with the inverse of the anion periodicity, namely, x . In the following, we take the hole picture.

The on-site Coulomb interaction term is treated within the mean-field approximation as $n_{i\uparrow} n_{i\downarrow} \simeq \langle n_{i\uparrow} \rangle n_{i\downarrow} + n_{i\uparrow} \langle n_{i\downarrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$ and self-consistent solutions are obtained at $T = 0$ for $\langle n_{i\sigma} \rangle$ ($\sigma = \uparrow, \downarrow$) on all sites in the supercell we take; we do not assume any functional form, e.g., a sinusoidal function for the charge and spin densities. We consider several choices for the anion periodicity $1/x$, such as, $x = 1/3, 2/5, 3/7$, and $4/9$, which are close to $x = 0.441$ but, to be exact, rational.

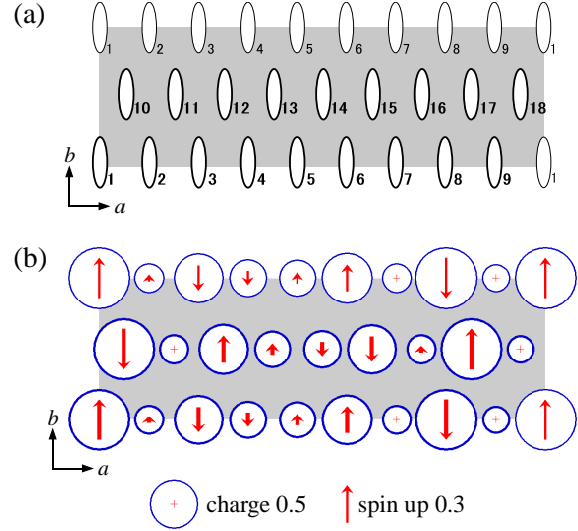


Fig. 3. (Color online) Supercell (a) and the distribution of charge and spin densities on each site in the mean-field solution (b) for $x = 4/9$. The gray rectangle is the supercell including independent 18 donor sites. Each sites is distinguished by the index shown in (a), which notation is also used in Figs. 4 and 5. In (b), the result for $U/t_a = 1.9$ and $\delta/t_a = 0.7$ is shown; the amount of charge density is expressed by the size of the circle, whereas the direction and the length of the arrow indicate up/down and the magnitude of spin moment. Reference scales are shown in the bottom.

This is due to a practical limitation that the size of the supercell has to be finite. We choose the supercells as 6, 5, 14, and 9 times the unit cell along the a -axis for the choices of x above, respectively, while that along the b -axis is unchanged. The main conclusions we reach below do not depend on the choice of x , therefore we expect that our results hold for purely IC systems as well.

In Fig. 2, the ground-state phase diagrams for the different values of x are shown, on the plane of the strength of the anion potential δ and the on-site Coulomb repulsion U , both normalized by the largest transfer integral t_a , that along the a -axis. In all cases, three distinct phases are obtained. The paramagnetic metallic (PM) phase exists for relatively weak δ and U , whereas the antiferromagnetic insulating (AFI) state is realized for strong δ and U . Between these two states, there appears an AF metallic (AFM) phase in which the Fermi surface partially remains even in the presence of the AF order. The transition between the PM and AFM phases is continuous, while a first order phase transition occurs between the PM and AFI phases, for all cases of x .

All the phase diagrams share common feature that the reduction of the band width and/or the enhancement of the anion potential leads to the insulating state: the on-site Coulomb repulsion U in the donor layer and the anion potential δ act cooperatively to give rise to the AFI state. This is analogous to the results in the simplified 1D model,¹⁷⁾ where the IC Mott insulator is stabilized when both U and δ are large; however, the strong fluctuation, which is significant in 1D, prevents the AF long-range order, and then its phase diagram has only two phases. It should be noted that effects of quantum fluctuation are neglected in the present mean-field treatment, so the regions of the AF ordering are overestimated.

We next show the distribution of charge and spin densities,

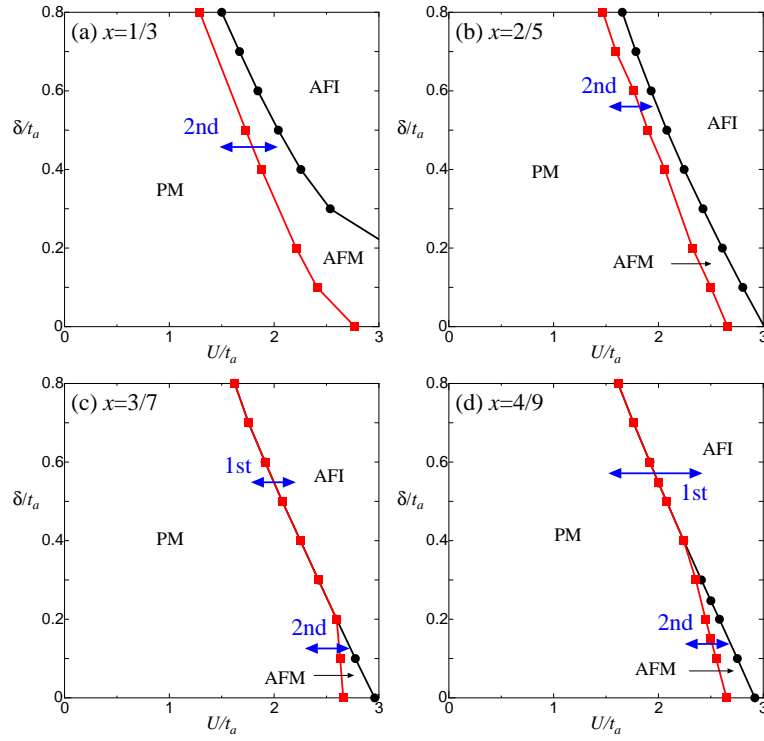


Fig. 2. (Color online) Ground-state phase diagrams obtained by the mean-field approximation for the two-dimensional model for (MDT-TS)(AuI₂)_x with $x = 1/3$ (a), $x = 2/5$ (b), $x = 3/7$ (c), and $x = 4/9$ (d). δ and U are the strength of the anion potential and the on-site Coulomb repulsion. PM, AFM, and AFI denote the paramagnetic metallic, antiferromagnetic metallic, and antiferromagnetic insulating phases, respectively. The paramagnetic-antiferromagnetic and metal-insulator phase boundaries are shown by a red curve with squares and by a black curve with circles, respectively, while “1st” (“2nd”) expresses the first (second) order phase transition.

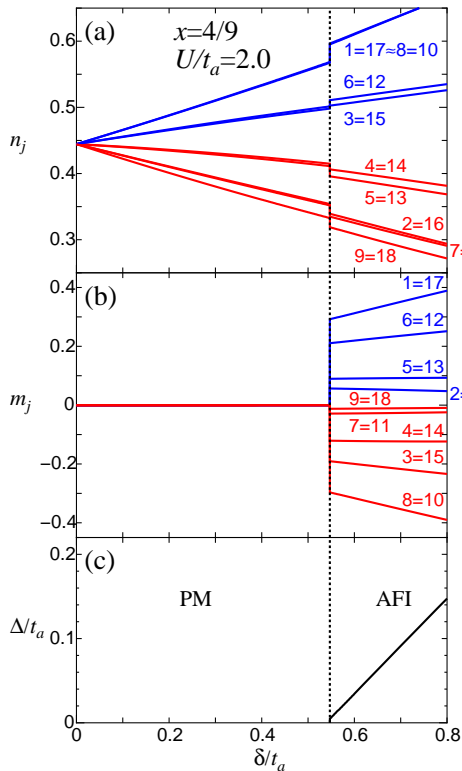


Fig. 4. (Color online) Charge (a) and spin (b) distribution and the charge gap Δ (c) for the case of $x = 4/9$, as a function of δ/t_a for fixed $U/t_a = 2.0$. The integers indicate site indices in the supercell as shown in Fig. 3.

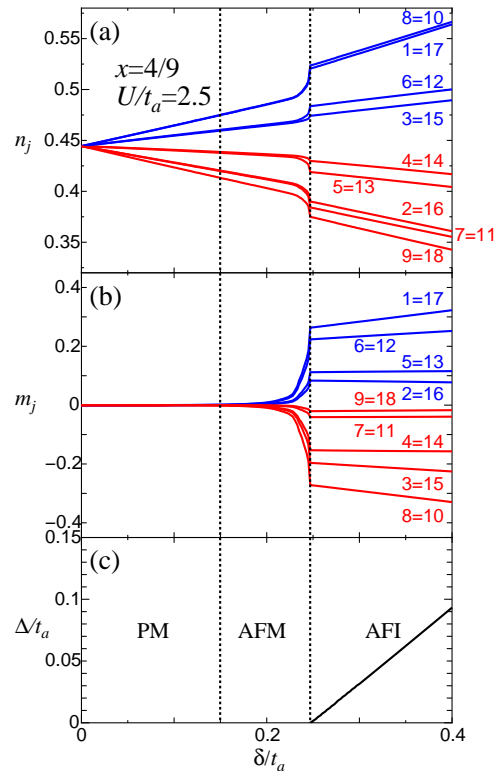


Fig. 5. (Color online) Charge (a) and spin (b) distribution and the charge gap Δ (c) for the case of $x = 4/9$, as a function of δ/t_a for fixed $U/t_a = 2.5$. The integers indicate site indices in the supercell as shown in Fig. 3.

in the case of $x = 4/9$, where there exist 18 donors and 8 carrier holes in the supercell [see Fig. 3 (a)]: The δ -dependences of the charge and spin densities at each site together with the charge gap, for $U/t_a = 2.0$ and $U/t_a = 2.5$ are shown in Figs. 4 and 5, respectively.

In the former case, the PM and AFI states are divided by the sharp first order transition. In the PM state, as seen in Fig. 4(a), the charge on each site is always disproportionated according to the anion potential.¹⁹⁾ When the first order transition sets in, the charge disproportionation is further enhanced; however, the symmetry in the charge sector is not lowered. The spin arrangement in the AF state can be understood as the Neel ordering of the spins localized at the charge rich sites: in Fig. 3 (b), the real-space configuration of the charge and spin pattern is shown. One can regard this pattern as effective $S = 1/2$ localized spins on each $9/4$ molecules, which is the anion periodicity $1/x$, forming a simple staggered AF pattern among 8 spins in the supercell.

In the case of $U/t_a = 2.5$ (Fig. 5), on the other hand, as increasing the anion potential the ground state first changes from PM to AFM, and then to the AFI state. As in the case of $U/t_a = 2.0$, the charge disproportionation exists even in the PM state and it is enhanced as δ is increased. The charge distribution does not show any clear singularities at the transition between PM and AFM. The charge pattern itself is always the same in the whole phase diagram; this holds for each of the x values we considered, namely, for all the phase diagrams shown in Fig. 2.

The AFI state we obtain can be interpreted as the IC Mott insulator which was predicted in the 1D model,¹⁷⁾ with which the magnetic ordering is accompanied in the present case. The periods of the charge and the spin densities do not match the donor lattice where the carriers exist, but follow the anion periodicity without changing the charge pattern from the PM state. These features are expected from the previous results in the 1D case: the charge is arranged according to the anion potential, and then the period of charge arrangement is IC to that of donors where the carriers exist. The translational symmetry is not broken in the transition to the IC Mott insulating state. The spin degree of freedom behaves as a Heisenberg localized spin, therefore as a spin liquid in the 1D model, which is expected to show AF order when the dimensionality effect is added, as in fact realized in the present calculation.

Let us note that the IC Mott insulating state should be distinguished from the charge ordered state widely observed in the A_2B -type molecular conductors. In the latter, the charge disproportionation occurs due to the long range component of the mutual interaction and then the translational symmetry is broken. We also note another difference between the 1D case and our result for the 2D case: The AFI state is stabilized in the 2D model down to $\delta = 0$, whereas in the 1D model finite δ is needed to give rise to the IC Mott insulator. The present result in the 2D case suggests the existence of nesting property stabilizing AF, but we cannot ignore the possibility that it is an artifact of our mean-field treatment; as mentioned above, mean-field approximation usually overestimates ordered states. Calculations incorporating quantum effects are left for future studies; our result that the IC AFI state is stabilized when δ and U are large presumably remains unchanged.

The obtained phase diagrams are consistent with the experimental results that applying pressure leads to the transition from the Mott insulating state to the metallic state,¹⁰⁾ since the pressure is expected to increase the bandwidth. An interesting problem to be explored would be whether the IC Mott insulating state survives just up to the superconducting phase, similarly to the half-filled cases such as in κ -ET₂X system. Another possibility is that a spin-density-wave phase appears between the IC Mott insulating and the superconducting phases, typically observed in quasi-1D systems such as TM₂X. The nesting induced spin-density-wave state might correspond to AF states that we obtained in the small δ and/or U region, although at the mean-field level we cannot distinguish it from the AF ordering due to the Mott insulating state.

In summary, we theoretically investigated the ground-state properties of (MDT-TS)(AuI₂)_{0.441} by studying a two-dimensional Hubbard model under a periodic potential due to the anions within mean-field approximation. Three kinds of states, PM, AFM, and AFI states were obtained, and the AFI state is stabilized when both U and δ are strong. This state is analogous to the incommensurate Mott insulating state obtained previously by the bosonization and renormalization group study in a one-dimensional model.¹⁷⁾

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- 19) Although the charge distribution is mostly determined by the anion potential on each site, the anisotropy in the transfer integrals as well as the anion potential on the surrounding sites also affect it, therefore even for the sites where the on-site potential is equal deviations of the charge density occur (for example sites “3” and “6” in Fig. 4(a)).